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POLYMERIZATION AND COPOLYMERIZATION OF UNSATURATED FATTY ACIDS AND THEIR ESTERS

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A SURVEY OF THE LITERATURE

Agricultural Research Service
United States Department of Agriculture

PREFACE

The Northern Utilization Research and Development Division, Peoria, Ill., under the administration of the Agricultural Research Service of the U.S. Department of Agriculture, is one of the four large research laboratories established by the Department under the authority of the Agricultural Adjustment Act of 1938. At its inception this laboratory was called the Northern Regional Research Laboratory.

The function of the several regional laboratories is to conduct chemical, chemical engineering, and other scientific investigations on new and broader uses of farm commodities and on the products from them. The commodities being investigated in the Northern Division are wheat, corn, and other cereal crops; soybeans and other oilseed crops (except cottonseed and peanuts); and new industrial crops.

The improvement of existing processes and the development of new processes for the increased industrial utilization of flax and flaxseed products are among investigations of the Oilseed Crops Laboratory of the Northern Division.

The increasing use of synthetic emulsion paints for coating exterior wood surfaces competes with linseed oil paints for this oil's last major market; before 1960, emulsion paints prepared from linseed oil have not had acceptable properties. To retain and increase this traditional outlet for linseed oil in the surface coatings field, more information was needed on the preparation and properties of polymers and copolymers of linseed oil in emulsion paint systems. Such a project was undertaken by Stanford Research Institute in 1959 through a research contract 12-14-100-4505(71) supervised by the Northern Division. The general objective of the contract was to conduct investigations that would produce polymeric products from linseed oil and reactive monomeric materials and to incorporate such polymers into emulsions suitable for exterior emulsion paints. The first phase of the Stanford contract was a critical survey of the literature on the polymerization and copolymerization of unsaturated oils and their derivatives with vinyl monomers. The Stanford search covers the years 1936-1959.

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POLYMERIZATION AND COPOLYMERIZATION OF UNSATURATED FATTY ACIDS AND THEIR ESTERS

A SURVEY OF THE LITERATURE

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INTRODUCTION

A literature survey covering the years 1936-1959 was conducted to obtain information on the polymerization and copolymerization of drying oils and acids or alkyl esters related to them. The references to all pertinent papers are given in the Literature Survey section beginning on page 20. From among the 320 references listed, only the most significant papers have been critically reviewed and cited in the text. The principal conclusions reached from this literature survey are:

1. Unsaturated fatty acids and their alkyl esters give only dimers or low polymers on homopolymerization.

2. Styrene can copolymerize with acids and esters containing conjugated dienoic unsaturation. Above 100° C., increasing proportions of Diels-Alder adducts accompany the copolymerization. At lower temperatures in the presence of free radical initiators, little or no Diels-Alder products are formed, but relatively less fatty acid or ester enters the copolymer with styrene.

3. Data on copolymerization of fatty acids and esters with styrene in emulsion, or with other monomers under any conditions, are inadequate to permit reaching any useful conclusions.

4. Because of the complications that arise in interpreting studies of the copolymerization of styrene with single acids and their methyl esters, it is even more difficult to derive useful conclusions from studies of either pure or mixed glycerides of fatty acids. Therefore, experimental work with the pure methyl esters of oleic, linoleic, linolenic, and eleostearic acids will be undertaken to determine the effects on polymerization and copolymerization

[1/] A report of work done under contract with the U.S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Northern Utilization Research and Development Division.

of these esters of catalyst, temperature, conjugation, Diels-Alder-type reactions, and isomerization during polymerization. Such information should lead to understanding and perhaps control of the reactions of glycerides.

SCOPE AND ORGANIZATION OF THE LITERATURE SURVEY

"Chemical Abstracts" was searched from 1936 through September 1959. Where indices were available, the following headings were used: styrene, vinyl acetate, vinyl alcohol, vinyl compounds, oleic acids, linoleic acid, linolenic acid, eleostearic acid, linseed oil, drying oils, acrylic acid (and its esters), methacrylic acid (and its esters), acrylonitrile, maleic anhydride, fumaric acid (and its esters), maleic acid (and its esters, $C_{19}H_{34}O_2$ and $C_{19}H_{32}O_2$). For the years 1958-1959, the indices were unavailable and the following sections of "Chemical Abstracts" were reviewed: Paints, Varnishes, Lacquers, and Inks; Fatty Oils, Waxes, and Detergents; and Synthetic Resins and Plastics.

The structural formulas of the acids discussed are:

Oleic $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

Linoleic $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Linolenic $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Eleostearic $CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH(CH_2)_7COOH$

α-Eleostearic is cis,trans,trans; β is all trans.

Linseed oil acids contain 9-38 percent oleic, 3-43 percent linoleic, and 25-58 percent linolenic acids, as well as small amounts of palmitic and stearic acids. Tung oil acids have 4-16 percent oleic, 0-1 percent linoleic, 74-91 percent eleostearic, and 4-5 percent saturated acids. Dehydrated castor oil acids contain 80-92 percent of a mixture of linoleic acids and conjugated 9,11-unsaturated acids, 0-9 percent oleic, and 3-7 percent linoleic (308).[2/]

2/ Underlined numbers in parentheses refer to especially pertinent references in the Literature Survey, p. 20. For complete coverage, refer to all references listed under a specific category in the Survey.

GENERAL CONSIDERATIONS

To utilize linseed oil in emulsion paints, we need to know whether linseed oil, its isomers, or simple oxidation products can be either polymerized or copolymerized to polymers having moderate to high molecular weight. If such products are not obtained, then we need to know why so that new approaches to the problem may be tried. Since linseed oil is a glyceride containing a somewhat variable mixture of fatty acid residues, a study of methyl (or other alkyl) esters of representative unsaturated fatty acids, or of the free acids, promises to be much simpler and more readily interpreted. We shall therefore consider first the homopolymerization and then the copolymerization of the free acids and their alkyl esters; afterwards their glycerides and some other polyfunctional compounds will be considered.

ACIDS AND ESTERS OF MONOHYDRIC ALCOHOLS

Homopolymerization

Alkyl Esters

The literature gives no evidence that polymerizations of methyl esters of unsaturated fatty acids yield any high molecular weight polymers, either with or without addition of catalysts. Methyl eleostearate, when heated above 185° C. either in a carbon dioxide atmosphere or under vacuum, gives dimers and cyclic polymers (3, 18, 21), formed by an intermolecular Diels-Alder reaction (6, 20). With methyl linolenate at 230° C. Paschke and Wheeler (20) show that polymerization follows an apparent first-order reaction and that isomerization to a conjugated form appears to be the rate-determining step. On the other hand, in methyl stearate solution above 280° C., Rushman and Simpson (25) find that dimerization and development of conjugation in methyl linoleate are both second order with respect to ester. They report also that more dimer is formed from normal unconjugated linoleate than from its conjugated isomer. The presence of an anthraquinone catalyst increases the rates of both isomerization and dimerization.

Information is lacking on the behavior of esters of unsaturated fatty acids at lower temperatures, with or without catalysts. In addition, the effects of such factors as conjugation and cis,trans isomerization on the rate of reaction and nature of product are incompletely understood for solvent systems and totally lacking for emulsion systems.

Fatty Acids

Almost all the work dealing with reactions of pure fatty acids by themselves is concerned either with oxidation or with polymerization complicated by oxidation. The acids are said to oxidize more rapidly than the corresponding esters (28, 80). Boiling eleostearic acid results in an intermolecular Diels-Alder condensation, with formation of dibasic acids containing cyclohexene rings (18).

Copolymerizations

Qualitative Considerations

There are three ways in which an unsaturated ester (or acid) may interact with a vinyl monomer (usually styrene):

1. Copolymerization.--In either thermal or peroxide-catalyzed polymerizations, polymer chains grow by addition of terminal free radicals to the double bonds of the unsaturated compounds present. The monomer unit that entered last then becomes the reactive center and adds to another monomer unit. When more than one kind of unsaturated compound is present and when both enter appreciably into the formation of polymer, then copolymerization occurs. When so little of an unreactive monomer enters a polymer chain that it cannot be reliably detected either by suitable analyses or by changes in physical properties of the product, then copolymerization is usually considered to be absent.

2. Chain Transfer.--In the commonest form of chain transfer, the polymer radical abstracts an atom (usually hydrogen or halogen) from some other molecule (transfer agent). Thus the polymer chain is terminated, but the kinetic chain continues by addition of monomer to the radical formed from the transfer agent. According to this scheme, one molecule of transfer agent will appear in each molecule of polymer. The effects of chain transfer can normally be observed in two ways: by analysis for transfer agent in the polymer or by the effect of chain transfer on molecular weight. However, in reactions of vinyl monomers with unsaturated fatty esters, the esters may react by either copolymerization or chain transfer or both. Molecular weight determinations are necessary for distinguishing between the two modes of reaction. In general, if the unsaturated ester reduces the molecular weight of the polystyrene formed and if only one ester unit appears in each polymer molecule, then the ester reacted almost entirely by chain transfer.

3. Diels-Alder Reactions.--Diels-Alder reactions are condensations of a conjugated diene with some other unsaturated molecule to give a cyclic 1:1 product. They proceed at rates which depend on the structure of the reactants, on their concentrations, and on temperature and pressure, but which are independent of added catalysts or inhibitors. Diels-Alder reactions proceed most readily when one, but only one, of the unsaturated compounds contains conjugated carbonyl or nitrile groups.

The qualitative considerations on interactions of unsaturated acids and esters with vinyl monomers suggest that considerable care in analyses of reaction products is necessary if the results are to yield reliable interpretations. Copolymerization of unsaturated esters with styrene is, in general, a difficult process, as evidenced by the number of investigators who found it necessary to use high temperatures and to add the styrene slowly to the hot oil to avoid formation of polystyrene. Under such conditions, the ratio of unreacted styrene to unreacted ester during reaction is unknown, and the results add little to our understanding of the reactions.

One experiment of Hamann and Mauz (74) deserves mention even though they employed a mixture of "linseed oil acids." They refluxed a mixture of 25 percent of these acids, 25 percent styrene, and 50 percent xylene for 30 hours and made rather careful analyses of the products. They found both polystyrene and copolymer containing from 3 to 5 mole percent of fatty acids. From this and other experiments they conclude that much of the styrene reacted by chain transfer at 140° C., but that copolymerization is favored by higher temperatures and slow mixing of styrene with fatty acid.

Table 1 summarizes the most useful results we have found on the copolymerization of styrene with the specified unsaturated acids and esters. The principal virtues of these experiments are that they all started with a known ratio of styrene to acid or ester and that a relatively pure acid or ester was apparently employed. A plus sign (+) signifies that the author reported finding the indicated product; a minus sign (-) that he found it to be absent.

There is general agreement (7, 11, 12, 104) that the conjugated esters and acids have much more tendency than the unconjugated compounds to enter copolymers. At temperatures of 140° C. and above, half or more of the products are Diels-Alder adducts, when such products are sought by an adequate analytical method. In peroxide-catalyzed copolymerizations at 70° C., apparently little or no Diels-Alder products are formed (12).

TABLE 1.--Copolymerization of Styrene with Unsaturated Acids or Their Alkyl Esters

Type of compounds	Styrene weight	Solvent weight [1]	Initiator [2]	Temperature	Time	Atmosphere	Products: Diels-Alder	Products: Polystyrene	Products: Polyester	Products: Copolymer	Reference number
1 C=C	Percent	Percent	Percent	° C.	Hours						
Oleic acid-------	50	0	0	160-225	5-6	Reflux				+	81
Me oleate--------	50	0	1 Bz_2O_2	70	24?	-		+		-	12
Me oleate--------	25	50 Xylene	1-10 Bz_2O_2	140	16	Reflux		+		-	11
Me elaidate------	25	50 Xylene	1 Bz_2O_2	140	16	Reflux		+		-	11
Me ricinoleate---	25	50 Xylene	5 Bz_2O_2	140	16	Reflux		+		-	11
2 C=C											
Me 9,12-linoleate	25	50 Xylene	1-10 Bz_2O_2	140	16	Reflux				-	11
Me trans,trans-10,12-linoleate	25	50 Xylene	1-5 Bz_2O_2	140	16	Reflux				-	11
Me 9,11-linoleate	33	33 Xylene	0	140	168	Vacuum	+	+	+		7
Me 9,11-linoleate	50	0	0	140	168	Vacuum	+		+	+	7
Me 9,12-linoleate	33	33 Xylene	0	140	240	Vacuum	-	+		-	7
Me linoleate-----	50	0	2 Bz_2O_2	70	24?	-				+	12
Me trans,trans-10,12-octadecadienoate	50	0	2 Bz_2O_2	70	24?	-				+	12
3 C=C											
Me linolenate----	50	0	2 Bz_2O_2	70	24?	-				+	12
Me linolenate----	33	33 Xylene	0	140	168	Vacuum	-	+[3]	+	-	7
Me α-eleostearate	33	33 Xylene	0	140	105	N_2	+		+	+	7
Me α-eleostearate	33	33 Dipentene	0	140	138	N_2	+		+	+	7
β-Eleostearic acid	25	50 Xylene	0	140	?	N_2	+			+	62

1/ Wt. % oil is difference [100 - (wt. % C_8H_8 + wt. % solvent)].
2/ On weight of styrene.
3/ Polystyrene may have contained one ester end group.

TABLE 2.--Copolymerization of Styrene and Methyl Alpha-Eleostearate (7)

Solvent	Grams of ester[1]		Average moles of ester present	Moles of ester in copolymer	Grams of styrene[1]		Average moles of styrene present[1]	Moles of styrene in copolymer	r_s[4]
	Initial	Final[2]			Initial	Final[3]			
Xylene-----	59.8	13.6	0.126	0.0568	59.8	24.8	0.406	0.253	1.07
Dipentene--	56.6	16.9	.126	.0524	56.6	18.6	.361	.297	1.62

1/ Per 100 g. reaction mixture worked up.
2/ From higher boiling products by difference.
3/ Styrene not accounted for in products, by difference.
4/ Relative reactivity of styrene/ester toward styrene radicals by equation 2.

When an effort is made to draw more exact conclusions, the inadequacies of the data become more apparent. From the 79 percent to 99 percent recoveries of unreacted esters from reactions with styrene, Falkenburg, Hill, and Wolff (11) concluded that "no reaction takes place between styrene and fatty acid radicals." Nevertheless, the range in the recoveries suggests that some reaction occurred with some esters. In the work of Armitage and Kut (62) with β-eleostearic acid, it is not clear whether the conversion of styrene was complete or unspecified. In either case, comparison of their results with those of others is precluded. Further, their separation of Diels-Alder adducts from other polymers seems to have been incomplete.

Powers (81) reported that styrene copolymerizes with a nearly equal weight of oleic acid. This result is not consistent with the reports of others. He made no effort to analyze for Diels-Alder products; neither did he establish the reliability of his analytical method with known mixtures.

The work of Crofts (7) and of Harrison and Tolberg (12) is more nearly quantitative and will be treated therefore under "Quantitative Considerations."

Data for monomers other than styrene are scanty. The butyl α- or β-eleostearates give Diels-Alder adducts with acrylonitrile (15) and fumaronitrile (15). The corresponding acids also give Diels-Alder adducts with maleic anhydride (67, 188), as well as with both nitriles (188). No indication of high copolymers was found.

Unsaturated aliphatic compounds which do not polymerize alone have given copolymers of high molecular weight with maleic anhydride (304) and, presumably, unsaturated fatty acid residues will behave similarly. The best conditions are apparently near or below 100° C. in the presence of a free radical initiator. However, at higher temperatures this chain copolymerization is partly or largely replaced by a nonchain reaction. Then the reactive allylic C-H bond in the unsaturated grouping adds to maleic anhydride to give substituted succinic anhydrides without loss of unsaturation in the hydrocarbon residues. Methyl oleate reacts in this manner with excess maleic anhydride at 220° C. to give four isomeric substituted succinic anhydrides (2). (Methyl oleate has two kinds of allyl hydrogen atoms, and the two resulting allyl radicals can react in four ways.) Teeter and coworkers (26) carried out similar reactions between methyl linoleate and itaconic or citraconic anhydrides. Since some polymeric material was obtained, the addition of allylic hydrogen atoms must have been

accompanied by some copolymerization. The latter reaction was favored by the presence of dimethylaniline. Plimmer (22) has also reported condensation of methyl oleate, methyl linoleate, and linoleic acid with maleic anhydride at 180° C. or 220° C., accompanied by some decarboxylation.

Thus three types of reaction are possible between maleic-anhydride and unsaturated compounds. Further study may reveal that this account is oversimplified.

Quantitative Considerations

1. Theoretical Basis.--This section provides the quantitative basis for comparing the behavior of unsaturated esters in copolymerization and chain transfer. Detailed discussions of copolymerization are given elsewhere (304, 319); here it will suffice to outline the methods for calculating and applying of monomer reactivity ratios. In a free radical copolymerization of styrene and an ester, for example, the free valences in the growing polymer radicals must be associated with either styrene or ester units; the number and kinds of other units attached to these terminal units are usually unimportant. The composition of the copolymer being formed, $d[S]/d[E]$, is related to the composition of the unreacted monomers (feed) at the same instant through the monomer reactivity ratios, r_s and r_e, and the copolymerization equation may be expressed as:

$$\frac{d[S]}{d[E]} = \frac{[S]\left(r_s[S] + [E]\right)}{[E]\left(r_e[E] + [S]\right)} \qquad (1)$$

where r_s is the relative reactivity of styrene and ester toward a styrene radical (radical ending in a styrene unit) and r_e is the relative reactivity of ester and styrene toward an ester radical. [S] and [E] must be in moles, but since they always occur as ratios, volumes are unimportant. Equation 1 applies as long as [S]/[E] remains constant or as long as the average ratio of [S]/[E] gives a satisfactory approximation. The r_s and r_e are defined in such a way that $r > 1$ indicates a preference of a radical chain ending in a given monomer unit to react with the same monomer, etc. Since the r values are ratios of rate constants, they are dependent on temperature, but not on solvent or feed composition. If d[E] includes ester reacting by both copolymerization and chain transfer, then so do r_s and r_e.

In the systems under consideration, r_e is indistinguishable from zero experimentally, i.e., a polymer chain ending in an ester radical almost never adds to an ester monomer. Under these conditions, equation 1 becomes simply:

$$\frac{d[S]}{d[E]} = \frac{r_s [S]}{[E]} + 1 \qquad (2)$$

At high conversions, where average values of [S]/[E] are no longer applicable, then the integrated form of equation 2 applies

$$\log \frac{[E]}{[E]_o} = \frac{1}{r_s - 1} \log \frac{(r_s - 1)\frac{[S]_o}{[E]} + 1}{(r_s - 1)\frac{[S]}{[E]} + 1} \qquad (3)$$

Here the concentrations with subscripts refer to initial concentrations of reactants, and the other concentrations are those when the reaction was stopped and the polymer (or unreacted monomers) was analyzed.

In the work of Harrison and Tolberg (12) molecular weight data permit independent determination of chain transfer. The applicable equation is (302)

$$\frac{1}{\bar{P}} = C \frac{[E]}{[S]} + \frac{1}{\bar{P}_o} \qquad (4)$$

Here, $\bar{P}$ and $\bar{P}_o$ are the degrees of polymerization of polystyrene formed in the presence and absence of ester. The transfer constant, C, measures the effect of ester in depressing the molecular weight (increasing $1/\bar{P}$) of the polymer formed. [E]/[S] must be a mole ratio, and the equation is applicable in a given experiment only as long as [E]/[S] is constant, or as long as an average value is applicable. Equation 4 was developed for the thermal polymerization of styrene, but it applies to a series of catalyzed polymerizations when the ratio of monomer to initiator remains constant (297).

2. Experimental Results in Bulk or Solution.--Crofts (7) studied the interaction of styrene with the methyl esters of unsaturated acids at 140° C. by mixing equal weights of styrene, ester, and diluent (xylene or dipentene). Because these reactions were carried to too high conversions, large amounts of Diels-Alder products may have confused the results. Since the total grams present in each fraction of the product is not indicated in the article, in order to apply equation 2, we have assumed that all the methyl ester was recovered in some form and that all the combined styrene was recorded in the analyses, so that unreacted

styrene monomer can be calculated by difference. If the Diels-Alder product was separated adequately from the copolymers, then in the xylene experiment about 49 percent of the ester appeared in Diels-Alder products. It is therefore impossible to use the integrated equation 3 in spite of the high conversion levels. This situation requires the use of equation 2 and use of average relative concentrations of styrene and ester in the reacting solution. Table 2 shows that the r_s values thus obtained are similar in both xylene and dipentene solutions. They indicate that styrene is only slightly more reactive than ester. This result is inconsistent with almost all other indications.

There are other complications in these calculations. In the xylene experiment, the recovered ester was only 22 percent eleostearate and 78 percent esters of less unsaturation. If all these less unsaturated esters were present initially, then r_s will be still closer to one. Further, if the final reaction mixture really contained 41.4 percent of the initial styrene, even after 104 hours at 140° C., as we have assumed from the styrene not accounted for, then marked retardation of polymerization is indicated. Similar difficulties arise in the dipentene experiments. The indicated high proportion of unreacted styrene and the low calculated r_s both suggest that something is seriously wrong with Crofts' data or with our assumptions. Perhaps either styrene dimers or trimers or even Diels-Alder products have been missed in some of the fractions.

Harrison and Tolberg (12) provided the best data for calculations. They employed equal weights of styrene and methyl esters and 1 percent of benzoyl peroxide at 70° C. They also carried out satisfactory tests of their analytical method. We have made two assumptions for the calculations below: that their fig. 1 shows the conversion of styrene only and that their analyses in their Tables 1 and 2 refer to 24-hour products. Their results and our own calculations are summarized in our Table 3. All the esters reduce through chain transfer the molecular weight of the polystyrene formed. From this reduction we have calculated the transfer constant, C, for each ester. This constant is the relative reactivity toward polymer radicals of ester in chain transfer and of styrene in chain propagation. Since the latter rate is presumably constant in all experiments, the relative reactivities of the esters in chain transfer are directly proportional to their transfer constants. The last two esters, with methylene groups between vinyl groups, are nine times as reactive in chain transfer as the saturated and singly unsaturated esters. No more than one ester group can enter a polymer molecule by chain transfer, and the rest must enter through copolymerization.

TABLE 3.--Copolymerization of Styrene and Fatty Esters at 70° C.[1/]

[Experimental data of Harrison and Tolberg (12)]

Fatty ester or solvent	Styrene polymerized in 24 hours[3/]	Molecular weight of polymer	Number of groups per polymer molecule: Styrene	Benzoate	Ester	C[4/]	r_s[5/]
	Grams						
None[2/]	20.0	49,000	470	2.6	0		
Me stearate	9.5	39,000	370	1.8	0.64	0.00083	640
Me oleate	9.5	39,000	370	1.7	1.7	.00083	238
Me 10,12-octadecadienoate	8.6	40,000	340	2.5	14.5	.00093	17
Me alkali-conjugated linoleate	--	33,000	280	1.0	12.1	>.0029	--
Me linoleate	5.8	19,000	173	1.1	3.0	.0070	28
Me linolenate	4.0	13,400	125	.9	1.1	.0076	61

1/ 10 g. each of styrene and ester, 0.2 g. benzoyl peroxide.
2/ 20 g. styrene and 0.4 g. benzoyl peroxide.
3/ From fig. 1 in reference 12.
4/ Transfer constant of solvent from equation (4), taking $1/\bar{P}_o$ from first experiment.
5/ From equation (3); includes ester reacting by both chain transfer and copolymerization.

The analyses show that no stearate reacts by copolymerization (it cannot) and that little or no oleate nor linolenate react in this manner. The conjugated ester is 1/17, and the linoleic ester 1/28, as reactive as styrene in copolymerization at equimolar concentrations of the monomers. The integrated equation recognizes that the feeds initially contain 2.8 styrenes per ester and ultimately less than that amount at the ends of the runs.

Although this work is the best known to us, the data exhibit some inconsistencies if our assumptions are justified. In three cases, more than two end groups per polymer molecule are accounted for (benzoate and ester reaction by transfer) indicating either branching or errors in analyses or in molecular weights. The linolenate, with twice as high a concentration of active methylene groups, should be at least twice as reactive (have higher C) than the linoleate. Similarly, the linolenate with 50 percent more double bonds, should be more reactive in copolymerization (lower r_S), but it is not. Instead it seems to be a somewhat better retarder than the linoleate. Diels-Alder reactions and the unknown amounts of isomerization of unconjugated to conjugated esters accompanying chain transfer and polymerization may account for some of the difficulties. In any event, the data show that even the esters with conjugated unsaturation have little tendency to copolymerize with styrene at 70° C. The other esters have still less.

In general, r_S values tend to approach unity as the temperature is increased. Thus we may expect to incorporate more ester in polystyrene at higher temperatures and also to get more Diels-Alder products. Reliable data on monomers other than styrene are particularly needed.

3. Emulsion Polymerization.--Dyer and Maxwell (9) studied the emulsion polymerization of styrene and ethyl linoleate at 40° C. Since the linoleate was a mixture of 9,12- and 10,12-isomers, the results are not clear-cut. A feed containing 50 percent by weight of styrene, 11.5 percent of conjugated ester, and 38.5 percent unconjugated ester was polymerized for 16 hours under carbon dioxide. A 30-percent conversion to a copolymer containing 1 percent ester was obtained. A similar run under nitrogen for 21 hours gave a 21-percent conversion to copolymer containing 7.6 percent ester. The discrepancy between the carbon dioxide and nitrogen results leaves the reactivity of the esters in copolymerization unsettled. In the presence of either air or oxygen in a closed container, conversions were higher (46-50%), but the compositions were in the same range (1-4%). Preoxidized (and more conjugated) ester entered the copolymer more easily.

Because oxygen inhibits most emulsion polymerizations (303), the favorable effect of oxygen on the styrene-ethyl linoleate system raises the question as to whether a true emulsion polymerization or a suspension polymerization was involved. Since true emulsion polymerizations are characterized by much higher rates than can be obtained in bulk or solution, such comparisons are important. However, a suspension polymerization that would produce a fine suspension of polymer may well be useful for practical applications.

GLYCERIDES

Almost all the literature references on the copolymerization of styrene with unsaturated acids and esters involve glycerides. In most cases, no attempt was made to define the chemical composition of the glycerides, and the extent of copolymerization occurring was estimated from the clarity or homogeneity of the films obtained from the products. It was usually necessary to add the styrene gradually to the oil in order to obtain a copolymer and to avoid excessive formation of polystyrene. In typical examples, oxidized, bodied, or blown oils were mixed with styrene at high temperatures (140-500° C.) in the presence of air, and the products so obtained were described as being copolymers useful in coating materials, impregnating varnishes, printing inks, linoleums, plasticizers, adhesives, paints, emulsified oil products, air-drying or baking enamels, alkyd resins, and drying oils. Vinyl toluene has been employed in similar experiments (145). From an absorption spectroscopy study of the structure of oils and resins, Ahlers and O'Neill (104) concluded that conjugated oils form true copolymers with styrene while nonconjugated oils do not.

Radiotracer studies by Bobalek, Bradford, Leutner, and Akiyama (133) of analytical methods for styrenated castor oil (dehydrated) acids and tung oil fatty acids where the styrene was tagged with C^{14} have shown mostly that their methods for separating fractions were inadequate.

Bulk or Solution Polymerization

Numerous workers have refluxed various oils with styrene in xylene, with or without added benzoyl peroxide. The half-minute half-life of this initiator at 140° C. probably means that it has little effect except to confuse the analyses. In the earlier work, the formation of copolymers was reported (156, 160, 184), but as the analytical methods for investigating the products have improved, the presence of true copolymers has become less certain. Brunner and Tucker (144) studied the products of reaction of styrene and tung oil

(containing mostly eleostearic acid) in refluxing xylene. After saponification, their nonvolatile products consisted of 40 percent nonstyrenated acid, 40 percent of 1:1 styrene-acid (Diels-Alder) product, and 20 percent of polymer containing eight styrenes per eleostearic unit. It is not clear whether the polymer is a product of copolymerization, chain transfer, or a nonradical reaction or a mixture of such products. Petit and Fournier refluxed mixtures of about 45 percent styrene with 55 percent of linseed oil, linseed oil acids, or tung oil acids (232), without added solvent, at temperatures up to 250° C. They report finding only 1:1 products and polystyrene containing very small proportions of acid residues.

Emulsion or Suspension Polymerization

Samples of vegetable oils from various sources with different percentages of conjugation were reported as being copolymerized with styrene in aqueous emulsion at 75° C. by Bezman and Browning (127). Some samples were oxidized and heat-bodied before the reaction, and these showed a higher extent of copolymerization than the untreated oils. The copolymers were analyzed by spectrographic examination for carbonyl groups. With equal weights of styrene and linseed oil they found no copolymers at 75° C. However, after substantial preoxidation of the oil, about 5 percent of oil appeared in the copolymer. When the oil was first isomerized to conjugated glyceride without oxidation, no copolymerization was observed. Neither the peroxide value of the oil by itself nor conjugation by itself, could account for the extent of copolymerization observed in the emulsions. Our inference is that a combination of conjugated unsaturation (perhaps also involving carbonyl groups) and enhancement (by oxidation) of the solubility of the oil in the emulsion system might account for the observed copolymerization. In soybean oil experiments, they employed 70 weight percent of oil and 30 percent of styrene. At 75° C. they found a good correlation between the amount of oil in the copolymer and the peroxide value of the oil. Preoxidation of the oil in the presence of a cobalt compound, to reduce peroxide content and to increase viscosity of the oil, gave the most oil in the copolymer. In emulsion polymerization at 50° C., the proportion of oil (oxidized to peroxide value of 400) in the copolymer increased from 21 percent to 41 percent as the viscosity increased from 500 to 2,000 centipoises. These results are interpreted on the basis that almost all the oil enters the polymer by chain transfer and that the bigger the oil molecule, the more is incorporated per chain transfer reaction.

These experiments offer some hope of preparing polymerized linseed oil emulsions when the processes are better understood.

VINYL AND ALLYL ESTERS

The polymerization of vinyl esters of several unsaturated fatty acids has been studied (33, 40, 43, 45, 49, 50, 55). In general, the vinyl group is responsible for most of the polymerization, and unsaturation in the fatty acid residue tends to retard polymerization of the vinyl group (50). From the standpoint of information on drying oils, these experiments show mostly that copolymerization with monomers, such as vinyl acetate and vinyl chloride is likely to be retarded by the oils. Allyl esters seldom give high rates of homopolymerization or degrees of polymerization under any conditions. Port, Hansen, Jordan, Dietz, and Swern (50) showed that while vinyl esters of saturated fatty acids polymerize readily, as little as 5 percent of vinyl oleate has a marked retarding effect. Harrison and Wheeler (40) have shown convincingly why both vinyl and allyl esters of unsaturated fatty acids polymerize slowly and incompletely and also why the effect increases with unsaturation in the fatty acid. When the unconjugated acid residues react by chain transfer or when the conjugated residues react by addition, unreactive allyl radicals are formed that are unable to carry on the polymerization of the vinyl or allyl ester groups.

Dyer and Meisenhelder (36) studied the copolymerization of 2-chloroallyl linoleate with styrene, both in bulk and emulsion. From our standpoint, the most important conclusion is that most of the limited copolymerization which did occur involved the chloroallyl function (83 percent in one instance) and not the linoleate function.

Wilson and Pfau (30) found that sodium salts of linoleic and linolenic acids, when present in other saturated soaps, retard the emulsion copolymerization of styrene and butadiene although the conjugated linoleic salt does not. These observations suggest to us that chain transfer phenomena, which are not important in rates of bulk or solution polymerization, may have important rate effects in emulsion polymerization, where isolation of radicals in emulsion particles is important.

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